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EXAMINER	
LOUIE, MANDY C	

ART UNIT	PAPER NUMBER
1715	

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Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Office Action Summary	Application No.	Applicant(s)	
	10/584,642	MURAKAMI ET AL.	
	Examiner	Art Unit	
	MANDY LOUIE	1715	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE *3* MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *06/01/2011*.

2a)☒ This action is **FINAL**. 2b)☐ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) *1,3,5-8,11,12,15,16 and 18* is/are pending in the application.

4a) Of the above claim(s) *15,16 and 18* is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) *1, 3, 5-8, 11-12* is/are rejected.

7)☐ Claim(s) _____ is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12)☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☒ All b)☐ Some * c)☐ None of:

1.☒ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☒ Notice of References Cited (PTO-892)
2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☐ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date _____.
4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____.
5) ☐ Notice of Informal Patent Application
6) ☐ Other: _____.

DETAILED ACTION

Specification

1. The disclosure is objected to because of the following informalities: claim 1 has been amended (i.e. wherein partial pressure ratio of the titanium tetrachloride to ammonia in the first step is lower than that in the third step) to be consistent with partial pressure ranges of claim 3; however, in paragraph 0007 of the specification recites "the titanium tetrachloride to the ammonia in the first step is higher than that in the second step" which appears to contradicts to "partial pressure ratio in the first step is not less than 0.13 but less than 0.2 and the partial pressure ratio in the second step is not less than 0.2 but less than 1.5" of claim 3. It is requested that the term "in the first step is higher than that in the second step" in paragraph 0007 of the specification be changed to "in the first step is lower than that in the second step". Appropriate correction is required.

Claim Rejections - 35 USC § 103

1. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

The text of those sections of Title 35, U.S. Code not included in this action can be found in a prior Office action.

2. Claims 1, 3, 5 are rejected under 35 U.S.C. 103(a) as being unpatentable over Fiordalice [Us 5420072] in view of Ohto [US 20010035241], Foster [US 5567483], and Miyamoto [US 5840628].

As to claim 1, Fiordalice teaches a method for forming titanium nitride film on a substrate [title] by reacting titanium tetrachloride and ammonia [col 2, ln 65-67], the method comprising a first step of reacting titanium tetrachloride and ammonia with each other; thereby forming a first titanium nitride layer on the substrate [col 2, ln 61-68], where the supply of reaction gases is limited by a range of partial pressures that reacts within a predetermined chamber volume (supply limited region) [col 3, ln 19-26]; and a second step of reacting titanium tetrachloride and ammonia with each other; thereby forming a second titanium nitride layer on the first titanium nitride layer [col 3, ln 48-54]. Although the prior art does not explicitly teach the second step occurring in a reaction limited region, it would have been inherent to the prior art that the specified partial pressure ranges for the reaction gases and predetermined chamber volume of the second step would induce reaction at the substrate surface in a reaction limited manner (since the prior art teaches the second step requires a higher TiCl4 to NH3 partial pressure ratio [col 3, ln 20-22], the reaction of the second step is limited by how much TiCl4 can react with NH4 to form the second film, due to the higher TiCl4 partial pressure; therefore, the second step is reaction-limited by the potential chemical reactions that can occur between the two gases at the substrate). Fiordalice further exemplifies the partial pressure ratio of TiCl4/NH3 in the first step is lower (0.05mTorr of

TiCl4, 30mTorr of NH3; ratio of 0.00167) [col 3, ln 20-22] than of the ratio in the second step (11mTorr of TiCl4, 30mTorr of NH3; ratio of 0.367) [col 4, ln 11-13].

However, Fiordalice does not teach a second and a fourth step of annealing the substrate using N2 gas and H2 gas.

Ohto teaches a method of forming a metal nitride film [abstract] such as TiN [0001], where the method can comprise of repeating, alternatively and a predetermined number of times, a process of growing the metal nitride film on the substrate and thermally treating the metal nitride film [0017] in a gaseous atmosphere such as with ammonia [0016]. It would have been obvious to one of ordinary skill in the art to anneal each of the titanium nitride layers as suggested by Ohto. One would have been motivated to do so in order to form a titanium nitride film with excellent quality [0015]. However, Ohto does not teach using N2 gas and H2 gas for annealing.

Foster teaches a method of forming quality titanium nitride films [col 2, ln 20-25] where the method includes annealing the titanium nitride film in either nitrogen gas (N2) or ammonia gas [col 3, ln 42-54]. Therefore, it would have been obvious to one of ordinary skill in the art in light of Foster that nitrogen gas would be an operable and obvious variant for ammonia gas when annealing a TiN film.

However, the prior art does not teach the temperature of the substrate in the first step is lower than in the third step.

Miyamoto teaches the surface temperature of the substrate is preferably higher in the second step than in the first step [col 6, ln 50-54], which would further contribute to the reduction of chlorine (impurities) content [col 6, ln 54-56].

It would have been obvious to one of ordinary skill in the art at the time of the invention to optimize the temperature range (300-800 degrees Celsius, col 3, ln 3, 67) so that the substrate temperature is higher in the second step than the first step as suggested by Miyamoto. One would have been motivated to do so to reduce chlorine (impurities) content [Miyamoto, col 6, ln 54-56].

As to claim 3, Fiordalice teaches the range of the partial pressure ratio in the first step can be 0.0001-0.1 (TiCl4 partial pressure range/ NH4 partial pressure range) [col 3, ln 4-6] and the second step can be 0.003-10 [col 4, ln 1-2], where the claimed ranges "overlap or lie inside ranges disclosed by the prior art" a *prima facie* case of obviousness exists. (See MPEP 2144.05.I). Although prior art does not explicitly teach the claimed range for the partial pressure ratio in the first step, it would have been obvious to one of ordinary skill in the art to optimize the partial pressure ratio of the first step via routine experimentation, since Fiordalice teaches these parameters affect film properties of TiN (i.e. crystal orientation, col 3, ln 8-12).

As to claim 5, although Miyamoto does not explicitly teach the claimed temperature ranges for the first step and second step, it would have been obvious to one of ordinary skill in the art to optimize the surface temperature to these ranges via routine experimentation, since Miyamoto teaches such modification reduces chlorine content in the TiN layer [col 6, ln 54-56].

3. Claims 6-7 are rejected under 35 U.S.C. 103(a) as being unpatentable over Wang [US 20020064598] in view of Ohto [US 20010035241], Foster [US 5567483], and Miyamoto [US 5840628].

As to claim 6, Wang teaches a method of forming a TiN composite layer on a substrate [abstract] to be processed in a chamber [0024] through the reaction of titanium tetrachloride and ammonia [abstract], the method comprising: a first step of supplying titanium tetrachloride and ammonia into the chamber with flow rate ratio of the ammonia to the titanium tetrachloride (NH3/TiCl4 flow rate ratio) being a first rate ratio [0010] at a chamber pressure range greater than 5 Torr (greater than 666.6Pa) [0033] thereby forming a first titanium nitride layer on the substrate [0010], a second step of supplying titanium tetrachloride and ammonia into the chamber with flow rate ratio of the ammonia to the titanium tetrachloride (NH3/TiCl4 flow rate ratio) being a second flow rate smaller than the first flow rate [0010], while the chamber pressure is held at a range greater than 5 Torr (greater than 666.6Pa) [0037].

However, Wang appears to not teach a second and a fourth step of annealing the substrate using N2 gas and H2 gas.

Ohto teaches a method of forming a metal nitride film [abstract] such as TiN [0001], where the method can comprise of repeating, alternatively and a predetermined number of times, a process of growing the metal nitride film on the substrate and thermally treating the metal nitride film [0017] in a gaseous atmosphere such as with ammonia [0016]. It would have been obvious to one of ordinary skill in the art to anneal each of the titanium nitride layers as suggested by Ohto. One would have been

motivated to do so in order to form a titanium nitride film with excellent quality [0015]. However, Ohto does not teach using N2 gas and H2 gas for annealing.

Foster teaches a method of forming quality titanium nitride films [col 2, ln 20-25] where the method includes annealing the titanium nitride film in either nitrogen gas (N2) or ammonia gas [col 3, ln 42-54]. Therefore, it would have been obvious to one of ordinary skill in the art in light of Foster that nitrogen gas would be an operable and obvious variant for ammonia gas when annealing a TiN film.

However, the prior art does not teach the temperature of the substrate in the first step is lower than in the third step.

Miyamoto teaches the surface temperature of the substrate is preferably higher in the second step than in the first step [col 6, ln 50-54], which would further contribute to the reduction of chlorine (impurities) content [col 6, ln 54-56].

It would have been obvious to one of ordinary skill in the art at the time of the invention to optimize the temperature range (300-800 degrees Celsius, col 3, ln 3, 67) so that the substrate temperature is higher in the second step than the first step as suggested by Miyamoto. One would have been motivated to do so to reduce chlorine (impurities) content [Miyamoto, col 6, ln 54-56].

As to claim 7, Wang teaches the first flow ratio can be 40-250, and the second flow ratio can be 2.5-17, or 8.5 [0010]; where the claimed ranges "overlap or lie inside ranges disclosed by the prior art" a *prima facie* case of obviousness exists (See MPEP 2144.05.I).

4. Claim 8 is rejected under 35 U.S.C. 103(a) as being unpatentable over Wang in view of Ohto, Foster, and Miyamoto, further in view of Lee [US 20010002334].

Prior art is aforementioned, but appears to be silent in teaching the first step is in a range of 2.5-15. Lee remedies this.

As to claims 8, Lee teaches the first TiN layer can have a firs gas flow ratio of TiCl4 to NH3 from 0.02-0.1 (NH3/TiCl4: 10-50) [0064]. In the case where the claimed ranges "overlap or lie inside ranges disclosed by the prior art" a *prima facie* case of obviousness exists. (See MPEP 2144.05.I).

It would have been obvious to one of ordinary skill in the art at the time of the invention to modify the first gas flow ratio to the range taught by Lee. One would have been motivated to do so to lower the Cl component to yield a denser film [Lee, 0064] so deterioration rate of the semiconductor device is lower [Lee, 0032].

5. Claims 11-12 are rejected under 35 U.S.C. 103(a) as being unpatentable over Wang in view of Ohto, Foster, and Miyamoto, further in view of Yamamoto [US 20020006739].

Teaching of Wang is aforementioned and teaches the first and second titanium nitride layers are formed while the substrate is placed in the chamber in the first and second step [0025, 0030-0031], but appears to be silent in teaching the method further comprising a step of purging an interior of the chamber with a purge gas after at least one of the first and second steps. Yamamoto remedies this.

As to claim 11, Yamamoto teaches a method for forming TiN film onto a surface [abstract], wherein after forming the TiN film, a step of purging gas with an inert gas is provided [0020].

It would have been obvious to one of ordinary skill in the art at the time of the invention to provide a purging step at either after the first step or second step of forming the TiN layers. One would have been motivated to do so to so as to purge the film forming chamber of the gas mixture or unreacted gas [0020] to remove any desired gases or components from the chamber.

As to claim 12, Yamamoto teaches argon is a known inert gas that is suitable for purging [0018]; and therefore it would have been obvious to have used argon as the purge gas because such gas would have been operable to successfully purge unwanted gases from the chamber with limited adverse effects.

Response to Arguments

1. Previous objection to claim 1 (to include a supply limited region) is withdrawn due to applicant's amendments.

2. Previous objection to claim 19 is withdrawn due to cancellation.

3. Previous objection to paragraph 0009 of the specification is withdrawn due to application's amendments.

4. Previous 112 second paragraph rejection drawn to claim 20 is withdrawn due to cancellation.

5. Applicant's arguments with respect to claims 1, 3, 5-8, 11-12 have been considered but are moot in view of the new ground(s) of rejection necessitated by amendments (claim 1: addition of two annealing steps, partial pressure ratio constraints and substrate temperature limitations, and claim 6: addition of two annealing steps, and substrate temperature limitations).

Conclusion

1. No claim is allowed.

2. Claims 1, 3, 5-8, 11-12 are rejected for the reasons aforementioned.

3. Applicant's amendment necessitated the new ground(s) of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL**. See MPEP § 706.07(a). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the date of this final action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to MANDY C. LOUIE whose telephone number is (571)270-5353. The examiner can normally be reached on Monday to Friday, 7:30AM - 5:00PM EST.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Timothy Meeks can be reached on (571)272-1423. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/M. C. L./
Examiner, Art Unit 1715

/Timothy H Meeks/
Supervisory Patent Examiner, Art Unit 1715